

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
15 April 2004 (15.04.2004)

PCT

(10) International Publication Number
WO 2004/031739 A2

(51) International Patent Classification⁷: **G01N 17/04**

(21) International Application Number:
PCT/GB2003/004209

(22) International Filing Date:
30 September 2003 (30.09.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0222658.7 1 October 2002 (01.10.2002) GB

(71) Applicant (for all designated States except US): BAE
SYSTEMS PLC [GB/GB]; 6 Calton Gardens, London
SW1Y 5AD (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): HARRIS, Steven,

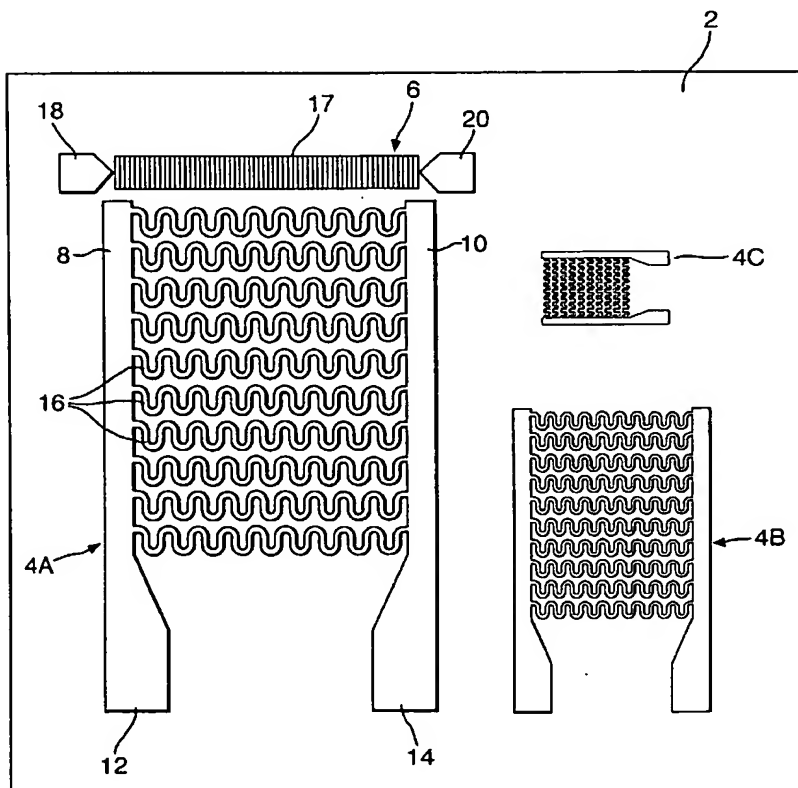
John [GB/GB]; Bae Systems ATC, SRC FPC 267, New Fil-
ton House, Filton, Bristol BS99 7AR (GB). HEBBRON,
Michael, Christopher [GB/GB]; Bae Systems ATC, SRC
FPC 267, New Filton House, Filton, Bristol BS99 7AR
(GB). STURLAND, Ian, Michael [GB/GB]; Bae Systems
ATC, SRC FPC 267, New Filton House, Filton, Bristol
BS99 7AR (GB).

(74) Agent: GROUP IP DEPARTMENT; BAE Systems plc,
Lancaster House, P.O. Box 87, Farnborough Aerospace
Centre, Farnborough, Hampshire, GU14 6YU (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE,
GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR,
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK,
MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT,
RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

[Continued on next page]

(54) Title: CORROSION SENSING MICROSENSORS



(57) Abstract: A microsensor for detecting corrosive media acting on a bulk metallic material when mounted in situ adjacent a location in the bulk metallic material. The microsensor includes a plurality of corrosion sensors (4A, 4B, 4C) exposed to the corrosive media, each having corrosion tracks formed from a patterned conductive thin film. The different sensors have different characteristics, such as track width, track thickness, track composition, surface type, sensor type, etc. so as to provide the sensors with different sensitivities, corrosion indications and lifetime characteristics. Such microsensor arrangements provide improved corrosion detection at high degrees of miniaturisation.



(84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

CORROSION SENSING MICROSENSORS

This invention relates to microsensors for detecting corrosive media acting on a metallic material when mounted in situ adjacent a location in
5 the metallic material.

Corrosion is a problem which leads to high maintenance and repair overheads in many different industries. The paper "Naval Aviation Corrosion Challenges and Solutions", Dale L. Moore, Corrosion 2000, paper 00270 (NACE, Orlando, USA, 2000) describes the problem areas in aircraft
10 component corrosion and classifies corrosion types found in the aircraft industry.

Various different methods of detecting corrosion in a metallic material are known. The paper "Corrosion Detection and Monitoring – a Review", Vinod S. Agarwala, Siri Ahmad, Corrosion 2000, paper 00271 (NACE, Orlando, USA,
15 2000) describes various of the known methods, including visual methods, ultrasonic and acoustic methods, radiographic methods, thermal imaging, electromagnetic methods, electrical resistance measurement, and electrochemical methods. It describes a commonly used type of corrosion sensing, referred to as the electrical resistance probe method. In this case a
20 sample of the material being monitored has its electrical resistance monitored. As the metal corrodes its cross section reduces and the resistance increases. In a practical embodiment of this technique the metal sample is made long and thin in order to optimise the resistance change to the thickness loss by corrosion. In this sensitive configuration the sensor is also highly sensitive to
25 temperature changes by virtue of the material's temperature coefficient of resistivity. This is often overcome by using a second sample of the material of identical dimensions and temperature but protected from corrosion. Even when all these features are accommodated this sensor type is poor when the
30 corrosion is at all localised, e.g. exfoliation, intergranular, pitting, crevice or stress corrosion. Under these conditions of degradation the resistance change is not proportional to extent of corrosion. Indeed it may not change sufficiently

- 2 -

to allow problematic corrosion to be reliably detected. Localised types of corrosion cause significant problems for some types of metallic materials such as aluminium alloys.

The paper "Multi-layer Galvanic Cell for Next Generation Corrosion Sensors", M.D. Jaeger, B.R. Pilvelait, P.J. Magari, Corrosion 2000, paper 00302 (NACE, Orlando, USA, 2000) describes a galvanic sensor with a multilayer geometry which is to be mounted in situ adjacent a location in a metallic material to be monitored and provides advantages in sensitivity and lifetime. The sensor measures the presence of an electrolyte, e.g. moisture in the area of the sensor, but not actual corrosion of the metallic material.

US patent 5338432 describes galvanic microsensors which use patterned thin metallic foils bonded to a non-conductive substrate. The sensors described include various alternative arrangements of interdigitated tracks of different metallic materials.

US patent 6383451 describes a thin film electric resistance sensor which includes a plurality of corrosive tracks exposed to corrosive media, running between two corrosion-protected common terminals. The detector described is sensitive to slight corrosion caused by pitting corrosion, however the current drain remains relatively high. In particular for corrosion monitoring in situ, it would be desirable to reduce the current drain in order to provide a longer battery lifespan; this is particularly important when a microsensor is to be mounted in a relatively inaccessible location and access thereto, for example for battery replacement, is to be avoided to as great an extent as possible. It would also be desirable to further improve the sensitivity and accuracy of the microsensor in detecting location-specific corrosion.

In accordance with one aspect of the present invention there is provided a microsensor for detecting corrosive media acting on a metallic material when mounted in situ adjacent a location in the metallic material, the microsensor including a plurality of different corrosion sensors, each said sensor having at least a part formed from a patterned conductive thin film and the different sensors being arranged to be differently influenced by corrosive

- 3 -

media in an area in which the unit is mounted, said microsensor providing a separate output derived from each of said sensors respectively.

The present invention provides a highly miniaturised microsensor which can detect corrosion with high accuracy and reliability, whilst a relatively
5 long lifetime of the microsensor is achievable.

Further aspects, features and advantages of the invention will become apparent from the following description of preferred embodiments of the invention given, by way of example, with reference to the accompanying drawings, wherein:

10 Figure 1 shows a microsensor arranged in accordance with a first embodiment of the invention, in plan view;

Figure 2 shows a more detailed plan view of the formation of corrosive tracks in the corrosion sensors of the microsensor shown in Figure 1;

Figure 3 shows a galvanic corrosion sensor conductive pattern
15 arrangement in accordance with an embodiment of the invention, in plan view; and

Figure 4 shows a referenced corrosion sensor pattern arrangement in accordance with an embodiment of the invention, in plan view.

Various different embodiments of microsensor in accordance with
20 the invention will now be described. The microsensors include corrosive tracks which mimic the corrosive characteristics of a bulk metal material, such that when placed in situ adjacent a location in a bulk metal material component, the effects of exposure to corrosive media measured by the microsensor reflect the effects of exposure of the bulk metal to the same corrosive media. The
25 microsensors may be mounted in various locations and manners, for example by mounting between the plates of a joint between components, by adhesion to a component using a Mylar™ foil, etc. Once mounted, the microsensors may be coated with paint or another type of coating which similarly covers the bulk metal material.

- 4 -

Figure 1 shows a microsensor element including a plurality of different corrosion sensors according to a first embodiment of the invention. The microsensor element includes a planar substrate 2 having an insulating surface provided for example by a layer of silicon oxide formed on a silicon base. The substrate 2 supports three thin film linear polarisation resistance (LPR) corrosion sensors 4A, 4B, 4C formed as thin film metallic patterns, and a thermocouple sensor 6 also formed as thin film metallic patterns. Each of the three corrosion sensors is formed of similar thin film patterns having similar geometries, except is formed of a different scale to the scale of the other corrosion sensors. For the avoidance of unnecessary repetition, the parts and functioning of only the largest corrosion sensor 4A are described in detail below, however it should be understood that each of the other corrosion sensors 4B, 4C has elements which are similar in arrangement and function to corresponding elements to be described, and the description of such elements should be taken to apply in relation to the other corrosion sensors also.

The largest corrosion sensor 4A includes two common terminals 8, 10 formed side-by-side in parallel strips on the substrate 2, ending in respective connector stubs 12, 14, across which an output signal is sensed. The common terminals 8, 10 may be made of a metal which is highly resistant to corrosion, such as gold or platinum, and/or may be covered in a protective thin film to prevent exposure of the common terminals 8, 10 to corrosive media.

Between the common terminals 8, 10, a plurality of conductive thin film corrosive tracks 16 are formed. The corrosive tracks 16 are not covered by a protective thin film, and are thus exposed to corrosive media, when the microsensor is in use, to a similar degree to which the bulk metallic alloy material, adjacent to which the microsensor is mounted, is exposed in the mounting location.

Figure 2 shows a more detailed plan view of the formation of the corrosive tracks 16. Each corrosive track has a width W which is substantially constant, preferably to within 10% of the width, across its length. As an exemplary value, the width W of each corrosive track may be selected to be in the region of 100µm in width.

- 5 -

Each corrosive track 16 is formed to meander across a separate surface portion, in this embodiment one of a set of linear corridors 20, between the common terminals 8, 10. The track 16 extends fully across the corridor 20 in which it meanders. The corridors 20 each have a similar width $D1$ and are
5 separated by a distance $D2$ such that the minimum separation $D3$ between adjacent corrosive tracks is preferably at least as great as the track width W . Each corrosive track 16 has a periodically repeating serpentine shape within the linear corridor. As can be seen in Figure 2, the corrosive tracks 16 are formed from alternately inverted generally U-shaped bends $B1, B2 \dots Bn \dots$ connected
10 by track sections $S1, S2 \dots Sn \dots$ spanning the centreline 22 of a corridor 20. The bends are alternately of opposite curvature. Each bend has a minimum radius of curvature R which is preferably greater than half the track width W . The spanning sections $S1, S2 \dots Sn \dots$ are spaced from each other such that the sides of adjacent spanning sections are spaced by a distance C at the
15 centreline, which distance is preferably greater than the track width W .

As a result of the serpentine shape of the corrosive track 16, the track gradually changes in direction, so that, using the centre line 22 as a reference axis, a track section of a positive or negative gradient relative to the centre line 22 is followed by a track section of an opposite gradient relative to the centre
20 line 22, the two sections being to each side of a bend of the corrosive track. The gradients alternately vary as the track is followed through each bend. The serpentine paths thus resemble a periodic waveform.

By providing a serpentine path such as that described, the track length is increased without the need to increase the microsensor dimensions
25 correspondingly, thus aiding miniaturisation. The sensitivity of the sensor is thus increased due to the increased track length and the current drain reduced. By using gradual bends having a minimum radius of curvature which is greater than half the track width as described, discrete or excessively sudden changes in direction of the path of the corrosive tracks, for example by the formation of
30 right angles in the track paths, are avoided. It has been found that accelerated corrosion phenomena occur at such points in the track paths, which undesirably

- 6 -

produce resistance variations which do not accurately reflect the state of corrosion of the component being monitored.

By maintaining at least a predetermined distance D3 between adjacent tracks, a predetermined minimum radius of curvature R at the bends, and at least a predetermined distance C between the adjacent track sections at the centre line, all track sections, including track sections within a single track and track sections within adjacent tracks, are well-spaced across the sensor. Preferably, no two adjacent track sections have sides spaced from each other by less than the track width W. In this way, corrosion effects are produced which more closely mimic the corrosion effects in the bulk alloy.

When mounted in situ, the effects of corrosion are monitored by intermittently passing a constant current across the common terminals and sensing the voltage response. After a period of exposure to corrosive media, whilst initially the tracking is fully intact and fully conductive, corroded track becomes gradually more resistive due to loss of conductive cross-sectional area and finally becomes insulating after corrosion affects at least one part of the track fully across its entire width. Different of the tracks may be affected differently by unrepresentative corrosive phenomena or other phenomena such as percussive damage, but by using a number of tracks, preferably at least four or more, connected in parallel, the response of the sensor more reliably reflects the effects of corrosion in the adjacent bulk metal.

The resistance thermometer 6 is made of a conductive material which is corrosively inert, such as platinum. The resistance thermometer 6 includes a tightly-concentrated sensing section 17 which provides well-behaved measurable variations in resistivity with temperature, formed between connector stubs 18, 20. Since rates of corrosion are highly temperature-dependent, the output from the resistance thermometer can be used in combination with the output from the corrosion sensor to provide more accurate corrosion state prediction for the bulk alloy material being monitored.

The microsensor may also include other types of sensor, not shown, for measuring parameters which can have an effect on corrosion rates, such as an

- 7 -

airflow sensor arranged for measuring airflow in the area in which the unit is mounted. Such an airflow sensor may be formed as thin film patterns of conductive strips, made of a material having a high temperature coefficient of resistivity, which are spaced in a direction in which airflow is to be sensed; variations in resistance of the strips indicate levels of airflow.

The second corrosion sensor 4B is in this embodiment formed of a scale which is half or less of the scale of the first and largest corrosion sensor 4A. The third corrosion sensor 4C is in this embodiment formed of a scale which is half or less of the scale of the second corrosion sensor 4B. More pronounced variations in scale are envisaged in a single microsensor element, for example a scale variation between any two microsensors may be such that one microsensor is one tenth or less of the scale of the other microsensor. The variations in sensor scale provide sensors with corrosive tracking of different widths in each sensor. By including the differently scaled sensors in a single microsensor unit the microsensor unit has a plurality of sensor outputs, derived from each sensor respectively, of different sensitivities to corrosion and with different sensor lifetimes. A sensor having a relatively small track width will be more sensitive but have a relatively small lifetime; the output from such a relatively small sensor may be used for monitoring corrosion during the early part of the life of the microsensor. Once the tracking of the relatively small sensor has degraded a sensor having a larger track width may be used to continue corrosion monitoring at a lower sensitivity during a subsequent period. When three or more sensors of different scales are used, once the output of the next smallest sensor has degraded a sensor having a larger track width may be used to continue corrosion monitoring at a still lower sensitivity during one or more further subsequent periods.

At any stage, corrective or preventive action may be taken as desired, in view of any perceived level of risk caused by the amount of corrosion detected at the location at which the corrosion is being monitored.

Figure 3 shows an alternative sensor pattern arrangement, for a galvanic corrosion sensor 130 arranged in accordance with one embodiment of the invention. One or more of the resistive sensors shown in Figure 1 may be

- 8 -

replaced with a galvanic corrosion sensor arranged as shown in Figure 3. For the avoidance of unnecessary repetition, elements which are similar in arrangement and function to corresponding elements shown in Figure 1 are referenced with the same numerals in Figure 3, except incremented by 100, and the previous description of such elements should be taken to apply here.

In this embodiment, the corrosion sensor 130 is in the form of a galvanic corrosion sensor having interdigitated thin film tracks 132, 134 formed of different metallic materials and producing a measurable variation in galvanic voltage in response to exposure to an electrolyte. The thin film tracks 132, 134 are not covered by a protective thin film and are thus exposed to an electrolyte, which is a corrosive medium such as moisture, when the microsensor is in use, to a similar degree to which the bulk metallic alloy material, adjacent to which the microsensor is mounted, is exposed in the mounting location.

The thin film tracks include a first set of thin film tracks 132 and a second set of thin film tracks 134. The first set are made from a first metallic material connected to a first common terminal 108 and not connected to the second common terminal 110. The second set of thin film tracks 134 are made from a second, different, metallic material connected to the second common terminal 110 and not connected to the first common terminal 108. Preferably, the first set of tracks 132 are formed from a corrosive material mimicking the bulk metal for which the microsensor is to be used to monitor corrosion, and the second set of tracks 134 are formed from a relatively corrosively inert metal such as gold or platinum. Thus, a galvanic voltage is generated between the common terminals by the sets of corrosive tracks 132 and the set of non-corrosive tracks 134, which is measurable to provide an indication of time of exposure and amount of exposure to the electrolyte in the bulk material.

The tracks 132, 134 are formed in the patterns described above in relation to Figure 2 in order to improve the performance of the sensor as described above.

Figure 4 shows an alternative sensor pattern arrangement, for a referenced corrosion sensor 130 arranged in accordance with one embodiment

- 9 -

of the invention. One or more of the resistive sensors shown in Figure 1 may be replaced with a referenced corrosion sensor arranged as shown in Figure 4. For the avoidance of unnecessary repetition, elements which are similar in arrangement and function to corresponding elements shown in Figure 1 are
5 referenced with the same numerals and further referenced A or B respectively in Figure 4, except incremented by 200, and the previous description of such elements should be taken to apply here.

In this embodiment, a corrosion sensor 204B having a similar form to the resistive corrosion sensor described in relation to Figure 1 formed with a
10 reference sensor 204A which takes substantially the same form and is made of substantially the same material or materials as the corrosion sensor 204B, but is covered by a protective thin film layer and is thus not exposed to corrosive media when the microsensor is in use. In manufacture, the reference sensor 204A is first laid down and formed, followed by the protective layer, followed by
15 the corrosion sensor 204B.

The corrosion sensor 204B is formed in an overlapping arrangement on top of the reference sensor. The function of the reference sensor 204A is to provide an output which is independent of corrosion but which has a virtually identical temperature-dependence in resistivity as the corrosion sensor 204B,
20 due to its similar patterning and composition. The output from the reference sensor 204A can thus be used to balance out any temperature dependence in the output of the corrosion sensor 204B in a simple manner. By arranging the two sensors in an overlapping manner, rather than side-by-side, the temperature of the corrosion sensor 204B and the reference sensor 204A are
25 more closely matched, in particular when mounted in locations subject to relatively large temperature gradients. Hence, the function of the reference sensor 204A is improved. Furthermore, miniaturisation of the microsensor element is improved.

The two sensors 204A, 204B are arranged with a slight offset, and the
30 corrosive tracks 216B and the corresponding tracks 216A are formed with a greater pitch. Thereby, the corrosive tracks 216B of the corrosion sensor are not formed on the surface of the protective film covering the corresponding

- 10 -

tracks 216A of the reference sensor; this avoids degradation of the uniformity of the corrosive tracks 216B due to variations in surface height of the protective layer due to the tracks 216A underneath. In this embodiment, the number of tracks in each sensor is half that of the sensor shown in Figure 1, which provides a microsensor element of similar size, however larger numbers of elements may be provided by increasing the length of the common terminals 208A, 210A; 208B, 210B.

Note that, in relation to Figures 1, 3 and 4, thin film wiring patterning, or other types of wiring, connecting the sensor connector stubs in a microsensor unit, although not shown, is to be understood to be added. Further, protective coatings are not shown in the Figures, although, as described above, may be used to selectively protect parts of the surface of the microsensor element.

In particular envisaged applications, the bulk metal material to be mimicked is a metallic alloy and in such cases the material used for the corrosive tracks in each of the above-described embodiments is preferably an alloy having alloying constituents in similar proportions to the respective bulk alloy being mimicked. It has been found that the proportion of each alloying constituent of the track material is generally preferred to be accurate within 3%, more preferably within 1%, of the total constituents of the bulk alloy. Constituents having a proportion of less than 1% of the bulk alloy may either be present in a similar proportion, or omitted.

In preferred embodiments, in which the microsensor is to be used in a health monitoring system for aircraft, the corrosive tracks are made of an aluminium alloy, such as an aluminium copper alloy, an aluminium silicon alloy, an aluminium silicon copper alloy, etc. In particular, the material used for the corrosive tracks is preferably an alloy which closely resembles in composition one of the aluminium alloys used in the aviation components.

In a first example the track alloy is an aluminium-copper alloy having a copper constituent proportion forming in the region of 2% to 8%, preferably approximately 5%, of the mass of the alloy, such as a 2000 series aluminium alloy.

- 11 -

In a second example the track alloy is an aluminium-silicon alloy having a silicon constituent proportion forming in the region of 5% to 20%, preferably approximately 12%, of the mass of the alloy, such as a 4000 series aluminium alloy.

5 In a third example the track alloy is an aluminium-magnesium alloy having a magnesium constituent proportion forming in the region of 2% to 8%, preferably approximately 5%, of the mass of the alloy, such as a 5000 series aluminium alloy.

10 In a fourth example the track alloy is an aluminium-magnesium-silicon alloy having magnesium and silicon proportions each forming in the region of 0.3% to 1.2% of the mass of the alloy, such as a 6000 series aluminium alloy.

15 In a fifth example the track alloy is an aluminium-zinc alloy having a zinc constituent proportion forming in the region of 2% to 8%, preferably approximately 5%, of the mass of the alloy, such as a 7000 series aluminium alloy.

In a sixth example the track alloy is an aluminium-lithium alloy having a lithium constituent proportion forming in the region of 1% to 4%, preferably approximately 2%, of the mass of the alloy, such as an 8000 series aluminium alloy.

20 Note that alloying constituents other than those specifically mentioned in each example above, and in lesser proportions to those specifically mentioned, may also be present in the alloys from which the tracks are made, particularly if present in the bulk alloys to be mimicked. These other alloying constituents may include one or more of magnesium, copper, manganese, silicon, iron, zinc,
25 lithium, titanium, chromium, vanadium, zirconium, etc.

The thin film layers from which the corrosive tracks are made is preferably deposited on the substrate by sputtering. In order to further improve the degree to which the corrosive characteristics of the thin film tracks mimic the bulk alloy, the thin film layer is preferably annealed following sputtering to
30 encourage growth of metallic grains within the thin layer to produce a thin film which is essentially a two-dimensional array of metallic grains. Enhancing the

- 12 -

grain size after sputtering by annealing enhances the capability of the sensors to specifically detect localised corrosion, at the early stages of its growth. Since localised corrosion initiates at specific sites such as grain boundaries, specific intermetallic phases etc, production of thin films of metal alloys with similar compositions of the intermetallic phases and grain boundaries of the bulk metal alloys concerned enhances detection of such localised corrosion. By subsequent photolithographic patterning, the films are structured into track forms, as described above, that give a desired sensitivity to such corrosion.

The thickness of the corrosive tracks is selected in accordance with the material from which the tracks are formed and the type of application for the microsensor. For example, for monitoring components in a marine environment the rate of corrosion is relatively high, and therefore a relatively thick film is used, for example, in the case of an aluminium alloy, corrosive tracks in the region of 50µm to 500µm in thickness are used. However, for other applications in which the environment in which the microsensor is to be placed is less corrosive, higher sensitivity to corrosion is required, and therefore thinner films are used to form the corrosive tracks. In the case of monitoring non-marine aircraft components, the thickness of the corrosive tracks is preferably between 0.5µm and 10µm, for example approximately 1.5µm.

The above-described geometries of the corrosive tracks may be used at any point in a range of miniaturisation scales. A track width of approximately 1µm is possible, and highly sensitive in the range of scales envisaged. However, such a track width will produce a sensor which is generally too sensitive for practical corrosion sensing applications. Track widths of up to 1mm are envisaged. Preferred track widths fall within the range 20µm to 500µm.

In one embodiment, not shown in the Figures, at least two of the different sensor configurations shown in Figures 1, 3 and 4 are formed on a single substrate, so as to provide a microsensor unit having a plurality of sensor outputs giving different indications of corrosion in a single location. For example, a galvanic corrosion sensor as described may be included to provide time-of-wetness data whilst a resistive corrosion sensor may be used to provide

- 13 -

an indication of actual corrosion which has been caused by the presence of corrosive media in the mounting location.

In a yet further embodiment, not shown in the Figures, sensors having tracking arranged as described and of a plurality of different thicknesses are formed on a single substrate and included in a single microsensor unit, so as to provide a microsensor unit having a plurality of sensor outputs giving different sensitivities to corrosion and different sensor lifetimes.

In a yet further embodiment, not shown in the Figures, sensors having tracking arranged as described and of a plurality of different metallic compositions, each preferably sharing at least the main metallic constituent of the bulk alloy being monitored, of different corrosivities are formed on a single substrate and included in a single microsensor unit, so as to provide a microsensor unit having a plurality of sensor outputs giving different sensitivities to corrosion and different sensor lifetimes. For example, in this case for monitoring aluminium alloy components, a first sensor having tracking made of a material which is relatively corrosive, such as an aluminium-silicon-copper alloy, may be included for higher sensitivity to corrosion but have a smaller lifetime, and a second sensor having tracking made of a less corrosive material such as substantially pure aluminium may be included for longer lifetime corrosion detection at a lower sensitivity. A third sensor having tracking made of a material having an intermediate corrosivity such as an aluminium-silicon alloy may also be included for medium lifetime corrosion detection at a medium sensitivity. The different tracks may also have different widths to provide preferred sensitivity and lifetime characteristics.

In a yet further embodiment, not shown in the Figures, sensors having tracking arranged as described and having a plurality of different surface types, for example one may be provide with a hydrophilic or hydrophobic surface treatment, to provide tracking of different sensitivities and lifetimes. The different sensors are formed on a single substrate and included in a single microsensor unit, so as to provide a microsensor unit having a plurality of sensor outputs giving different sensitivities to corrosion and different sensor lifetimes.

- 14 -

The corrosion microsensors described herein are located on various different components of a multi-component apparatus, such as an aircraft, to form a corrosion sensing system, which itself is part of a health monitoring system for the apparatus. Typically, the components of the apparatus will be
5 formed from different metal alloys, in particular, in the case of an aircraft, from different aluminium alloys such as the examples given above. One aspect of the invention is that a plurality of different corrosion microsensors, each having a set of corrosive tracks made of different metal alloy compositions mimicking the different component material compositions, are mounted adjacent locations
10 in the respective corresponding components to form part of the corrosion sensing system for the apparatus.

A corrosion sensing system arranged in accordance with the present invention includes a data processing system arranged to receive data derived from each of a plurality of microsensor units which contain the corrosion
15 sensors, to process the detection data and to provide corrosion analysis data based thereon, whereby corrosion state prediction is provided for the bulk alloy materials of the various different components in the various different locations being monitored. The units include a battery and a sensing circuit for each sensor. In the case of the LPR sensor, the circuit is adapted to apply a constant
20 current to common terminals of the sensor, and to measure a voltage generated therein to sense resistance changes in the sensor. In the case of the galvanic sensor, the circuit is adapted to sense the galvanic voltage generated across the two common terminals.

One or more of the corrosion sensors of the present invention may be
25 included in a semi-autonomous microsensor unit which includes a data logging memory, for storing sensor data sensed at a plurality of intervals over a period of time, and a data output whereby data is output from the microsensor unit to the data processing system. Such a semi-autonomous microsensor unit may be connected to the data processing system by means of physical wiring through
30 which data is communicated, or may include a data port whereby a data connection is intermittently established. The data port may be a socket to which

- 15 -

a data cable of a reader unit is manually connected, or a wireless data port such as a Bluetooth™ short range radio transmitter.

The above embodiments are to be understood as illustrative examples of the invention. Further embodiments of the invention are envisaged. Note for
5 example that, whilst the corridors across which the corrosive tracks extend are in the above-described embodiments linear, the corridors may instead take a different form, including various different curved forms, including bell-shaped forms. Whilst in the above embodiments, all of the conductive thin film parts of each of the corrosion sensors are formed on a single substrate in an alternative
10 configuration the microsensor includes conductive thin film parts of each of the different sensors which are formed on a plurality of different substrates, which may be bonded together.

Using thin film alloys to mimic the behaviour of bulk alloys lends itself to further applications in corrosion both to elucidate corrosion rates specific to
15 specific components and locations thereon, in which the microsensor is mounted. It should be noted that the invention is applicable to alloy systems other than aluminium, including magnesium alloys, which are used in the manufacture of gearbox components. It has particular benefit for alloys which tend to corrode locally, such as by exfoliation, or intergranular, pitting, crevice or
20 stress corrosion.

It should be understood that the above-described preferred geometries, in particular the track width values, the track section separation values and the minimum radii of curvature values, have been found by empirical observation. Experiments were conducted in which the corrosion rates of large numbers of
25 different test geometries were compared with the corrosion rates of the bulk metal materials being mimicked, when exposed to the same corrosive media. Geometries inside or outside the thresholds described were found to tend to cause corrosion effects which did not accurately reflect those in the bulk material; however it should be understood that, if different sensor characteristics
30 are desired, for example increased sensitivity to corrosion relative to the bulk material, such alternative geometries may be used.

- 16 -

It is to be understood that any feature described in relation to any one embodiment may be used alone, or in combination with other features described, and may also be used in combination with one or more features of any other of the embodiments, or any combination of any other of the
5 embodiments. Furthermore, equivalents and modifications not described above may also be employed without departing from the scope of the invention, which is defined in the accompanying claims.

- 17 -

CLAIMS

1. A microsensor for detecting corrosive media acting on a metallic material when mounted in situ adjacent a location in the metallic material, the microsensor including a plurality of different corrosion sensors, each said
5 sensor having at least a part formed from a patterned conductive thin film and the different sensors being arranged to be differently influenced by corrosive media in an area in which the unit is mounted, said microsensor providing a separate output derived from each of said sensors respectively.
2. A microsensor unit according to claim 1, wherein the plurality of corrosion
10 sensors comprise a resistivity sensor having a least one thin film track arranged to provide a measurable variation in resistivity in response to prolonged exposure to corrosive media.
3. A microsensor according to claim 2, wherein the plurality of corrosion
15 sensors comprise a plurality of resistivity sensors each having a least one thin film track arranged to provide a measurable variation in resistivity in response to prolonged exposure to corrosion.
4. A microsensor according to claim 3, wherein the resistivity sensors
include a first resistivity sensor having said at least one thin film track of a first width and a second resistivity sensor having said at least one thin film track of a
20 second, different width.
5. A microsensor according to claim 4, wherein said second width is a half or less of the first width.
6. A microsensor according to claim 5, wherein said second width is a tenth or less of the first width.
- 25 7. A microsensor according to any preceding claim, wherein the plurality of corrosion sensor include a corrosion sensor having at least one thin film track of a first thickness and a second resistivity sensor having at least one thin film track of a second, different thickness.
8. A microsensor according to any preceding claim, wherein the plurality of
30 corrosion sensors include a corrosion sensor having at least one thin film track

- 18 -

made of a first metallic composition and a different corrosion sensor having at least one thin film track of a second, different metallic composition.

9. A microsensor according to any preceding claim, wherein the plurality of corrosion sensors include a corrosion sensor having at least one thin film track having a first surface type and a different corrosion sensor having at least one thin film track of a second, different surface type.

10. A microsensor according to any preceding claim, wherein the plurality of corrosion sensors include a galvanic sensor having at least one thin film track made of a first metallic material and at least one further thin film track made of a second, different, metallic material, the tracks being arranged to provide a measurable variation in galvanic voltage in response to exposure to an electrolyte.

11. A microsensor according to any preceding claim, wherein the plurality of corrosion sensors include a referenced corrosion sensor including a resistivity sensor and a reference sensor arranged to provide a measurable variation in resistivity in response to changes in temperature, the reference sensor having similar temperature dependence to said resistivity sensor.

12. A microsensor according to any preceding claim, comprising a resistance thermometer sensor, a platinum resistance thermometer for example, arranged for measuring temperatures in an area in which the microsensor is mounted.

13. A microsensor according to any preceding claim, comprising an airflow sensor arranged for measuring levels of airflow in an area in which the microsensor is mounted.

14. A microsensor according to any preceding claim, wherein all of the conductive thin film parts of each of the corrosion sensors are formed on a single substrate having a surface formed from an insulating material.

15. A corrosion sensing system comprising a microsensor according to any preceding claim, wherein said system includes a data processor arranged to receive data derived from each of said separate outputs, to process said detection data and to provide corrosion analysis data based thereon.

Fig.1.

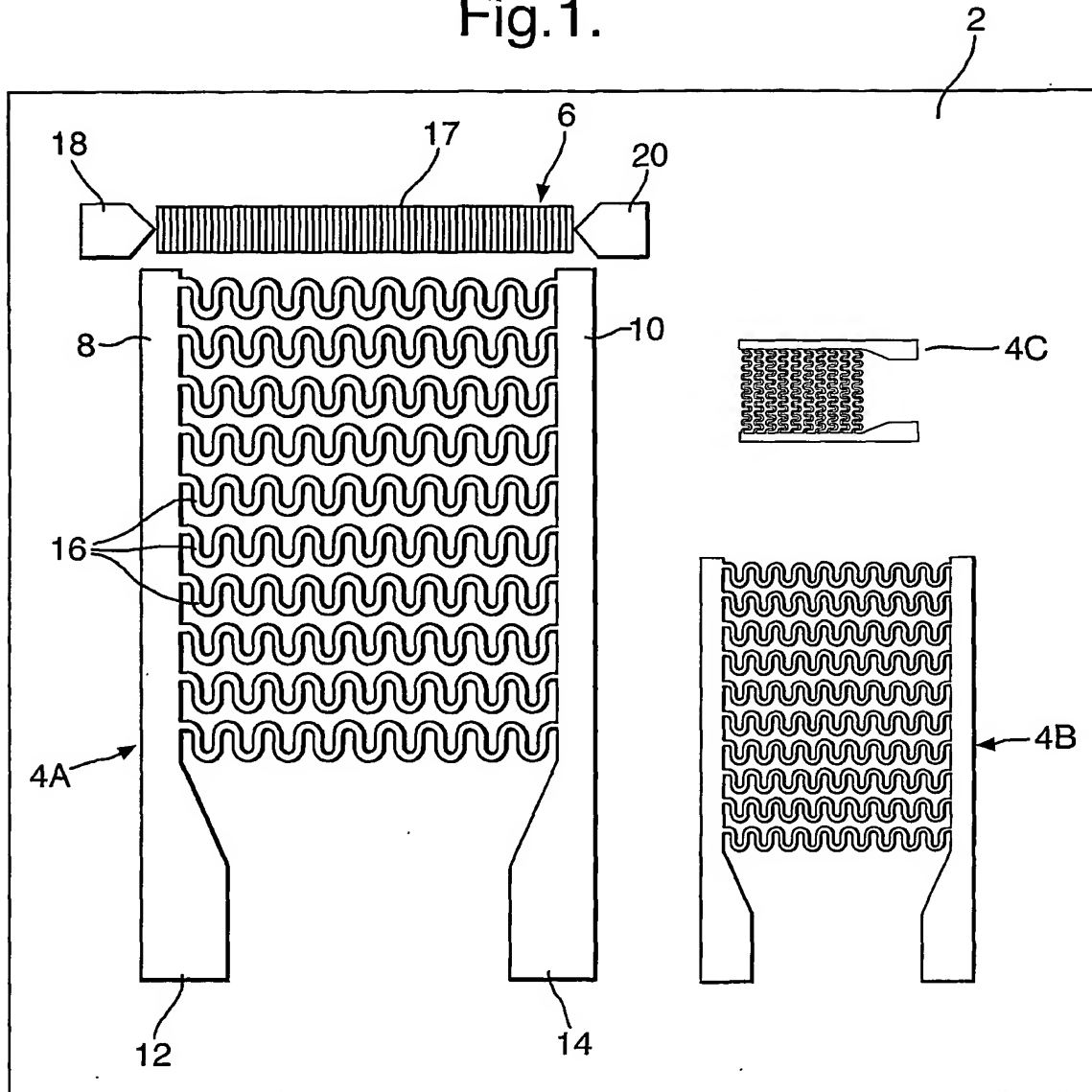
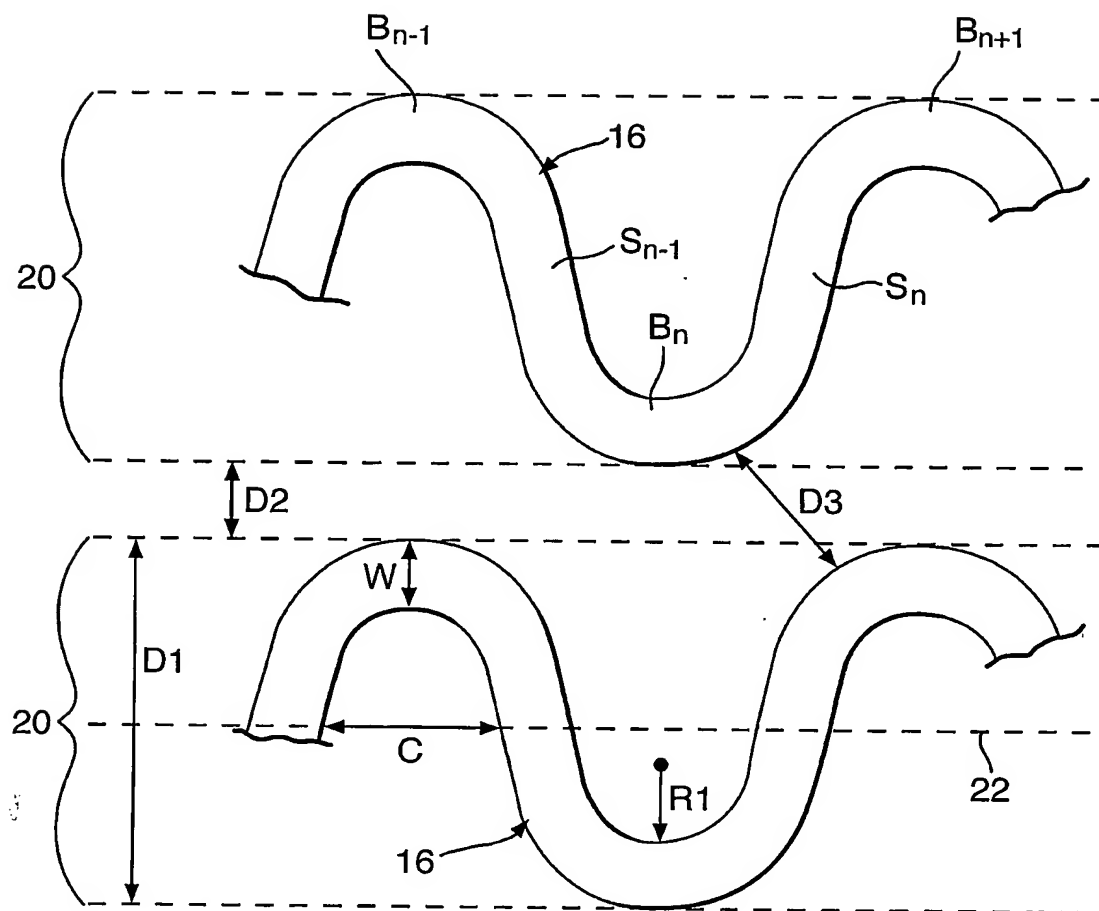


Fig.2.



10/529056

3/3

Fig.3.

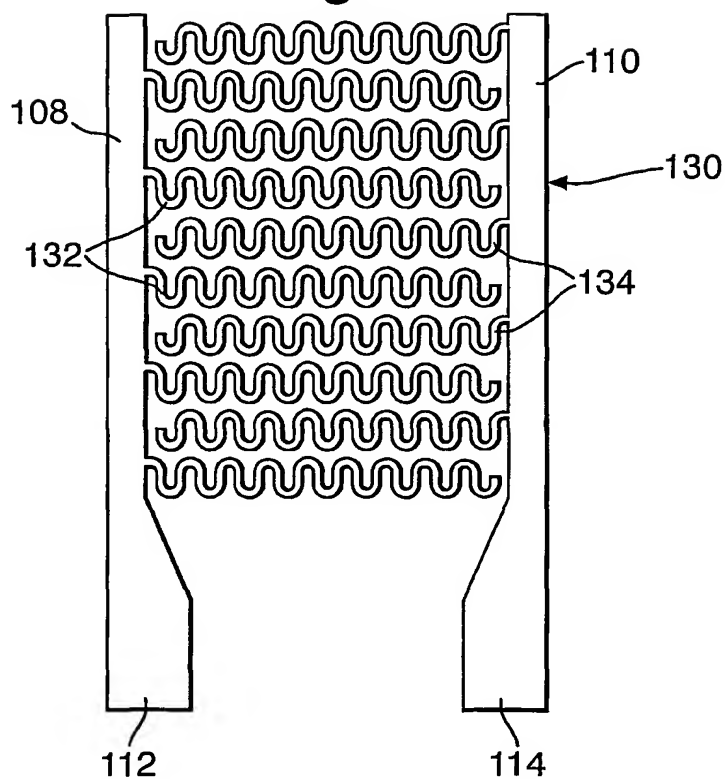
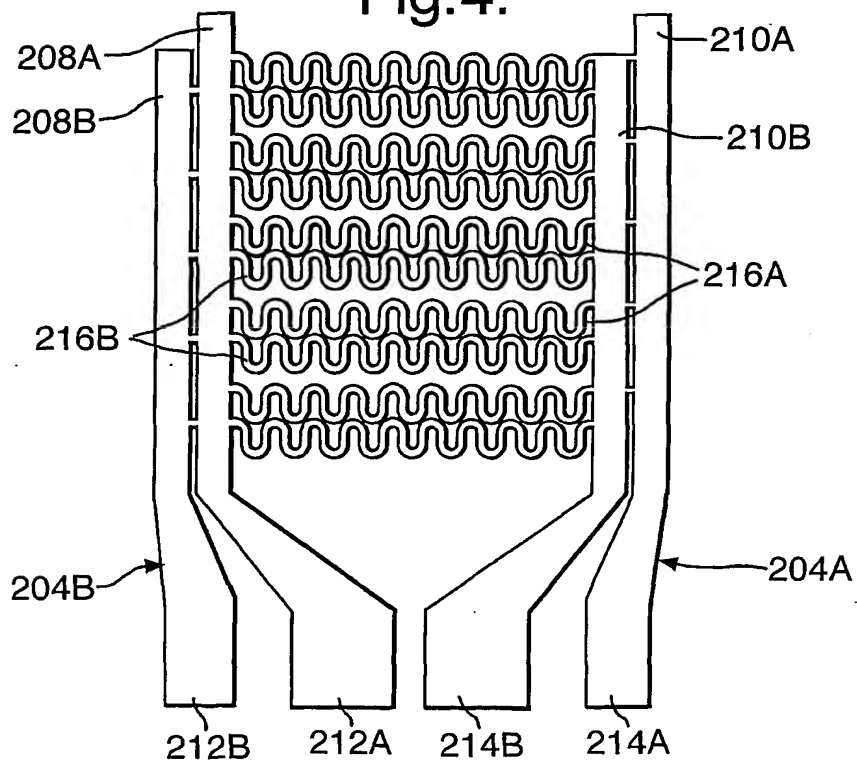


Fig.4.



(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
15 April 2004 (15.04.2004)

PCT

(10) International Publication Number
WO 2004/031739 A3

(51) International Patent Classification⁷: **G01N 17/04**

(21) International Application Number:
PCT/GB2003/004209

(22) International Filing Date:
30 September 2003 (30.09.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0222658.7 1 October 2002 (01.10.2002) GB

(71) Applicant (for all designated States except US): **BAE SYSTEMS PLC** [GB/GB]; 6 Calton Gardens, London SW1Y 5AD (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **HARRIS, Steven,**

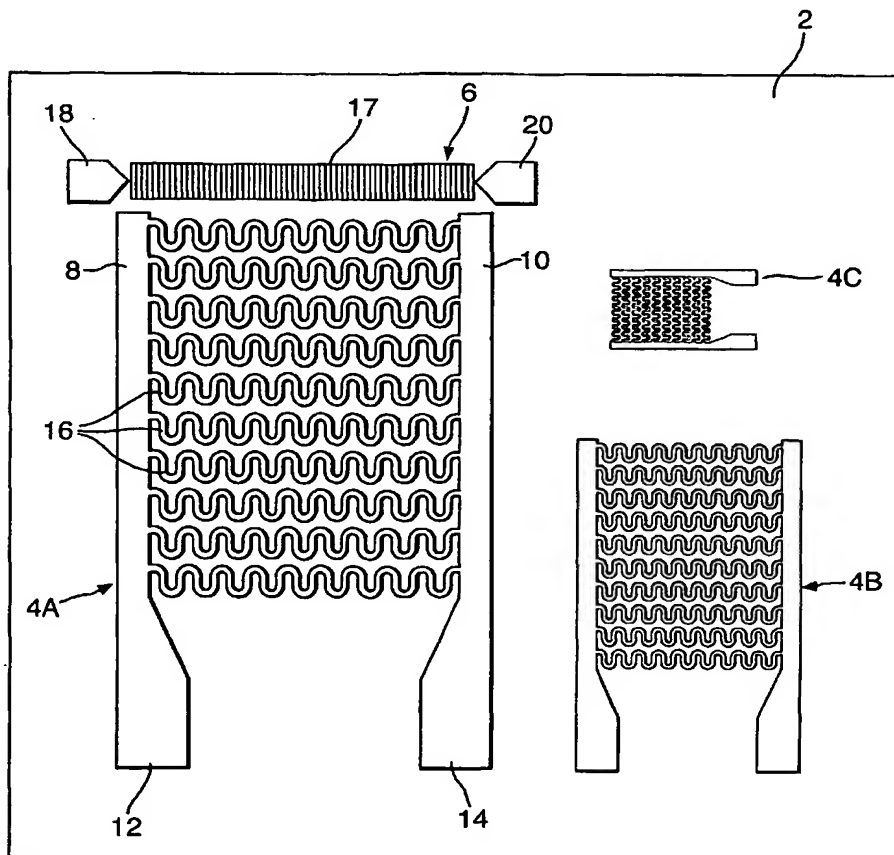
John [GB/GB]; Bae Systems ATC, SRC FPC 267, New Filton House, Filton, Bristol BS99 7AR (GB). **HEBBRON, Michael, Christopher** [GB/GB]; Bae Systems ATC, SRC FPC 267, New Filton House, Filton, Bristol BS99 7AR (GB). **STURLAND, Ian, Michael** [GB/GB]; Bae Systems ATC, SRC FPC 267, New Filton House, Filton, Bristol BS99 7AR (GB).

(74) Agent: **GROUP IP DEPARTMENT**; BAE Systems plc, Lancaster House, P.O. Box 87, Farnborough Aerospace Centre, Farnborough, Hampshire, GU14 6YU (GB).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

[Continued on next page]

(54) Title: CORROSION SENSING MICROSENSORS



(57) Abstract: A microsensor for detecting corrosive media acting on a bulk metallic material when mounted in situ adjacent a location in the bulk metallic material. The microsensor includes a plurality of corrosion sensors (4A, 4B, 4C) exposed to the corrosive media, each having corrosive tracks formed from a patterned conductive thin film. The different sensors have different characteristics, such as track width, track thickness, track composition, surface type, sensor type, etc. so as to provide the sensors with different sensitivities, corrosion indications and lifetime characteristics. Such microsensor arrangements provide improved corrosion detection at high degrees of miniaturisation.



(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:
19 August 2004

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

GB 03/04209

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N17/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 446 369 A (BYRNE MARK T ET AL) 29 August 1995 (1995-08-29) column 13, line 1 - line 48; figure 1	1-9,11, 12,14,15
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 08, 29 September 1995 (1995-09-29) -& JP 07 113740 A (HITACHI LTD), 2 May 1995 (1995-05-02) abstract; figures 1,2,4 paragraphs [0013],[0032] and claim 5	1,8,14, 15
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 495 (P-956), 9 November 1989 (1989-11-09) -& JP 01 197629 A (HITACHI LTD), 9 August 1989 (1989-08-09) abstract; figures 1-10	1,8-10, 14,15
	----- -/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

26 February 2004

Date of mailing of the international search report

24.06.2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Strohmayer, B

INTERNATIONAL SEARCH REPORT

GB 03/04209

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 009, no. 009 (P-327), 16 January 1985 (1985-01-16) -& JP 59 159061 A (MATSUSHITA DENKO KK), 8 September 1984 (1984-09-08) abstract; figure 1	1-9,14, 15
X	PATENT ABSTRACTS OF JAPAN vol. 009, no. 040 (P-336), 20 February 1985 (1985-02-20) -& JP 59 180433 A (TOSHIBA KK), 13 October 1984 (1984-10-13) abstract; figure 2	1,12,14, 15
X	CLIFFORD G. MOORE, BORIS MIKSIC: "INSTRUMENTATION FOR MEASUREMENT OF THE EFFECTIVENESS OF VAPOR CORROSION INHIBITORS" NACE, NATIONAL ASSOCIATION OF CORROSION ENGINEERS, CORROSION '95, [Online] no. 490, March 1995 (1995-03), pages 1-8, XP002271301 Orlando Retrieved from the Internet: URL: http://www.cortecvci.com/Publications/ Papers/VCIPProducts/CTP-15.PDF > [retrieved on 2004-02-25] page 2 - page 3	1-3,8, 11,15
X	US 4 780 664 A (HOWE ROBERT E ET AL) 25 October 1988 (1988-10-25) column 3, line 27 - line 53; figures 1,2	1-3,11, 14,15
P,X	US 2003/029232 A1 (DINWIDDIE RALPH B ET AL) 13 February 2003 (2003-02-13) paragraph [0007] - paragraph [0030]; figure 7	1-3,11, 14,15
A	US 5 338 432 A (AGARWALA VINOD S. ET AL) 16 August 1994 (1994-08-16) cited in the application column 3, line 40 - column 4, line 50; figures 1A,1B,1C,2	1,9,10

INTERNATIONAL SEARCH REPORT

PCT/GB 03/04209

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-12, 14, 15

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-12,14,15

1.1. claims: 4-6

The thin film tracks have different widths.
Problem to be solved: to provide an alternative way of arranging a plurality of thin film tracks to be differently influenced by corrosive media

1.2. claim: 9

The thin film tracks have different surface types.
Problem to be solved: to provide an alternative way of arranging a plurality of thin film tracks to be differently influenced by corrosive media

1.3. claim: 10

At least one thin film corrosion sensor is a galvanic sensor.
Problem to be solved: to provide an alternative type of corrosion sensor

2. claim: 13

An airflow sensor arranged for measuring levels of airflow in an area in which the microsensor is mounted.
Problem to be solved: to take airflow into account, which can have an effect on corrosion rates (application, paragraph bridging pages 6,7)

INTERNATIONAL SEARCH REPORT

International Application No

GB 03/04209

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5446369	A	29-08-1995	AU WO	5325094 A 9409354 A1
				09-05-1994 28-04-1994
JP 07113740	A	02-05-1995	NONE	
JP 01197629	A	09-08-1989	NONE	
JP 59159061	A	08-09-1984	NONE	
JP 59180433	A	13-10-1984	NONE	
US 4780664	A	25-10-1988	NONE	
US 2003029232	A1	13-02-2003	NONE	
US 5338432	A	16-08-1994	US	5310470 A
				10-05-1994